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BIOGAS PRODUCTION FROM ORANGE PEEL WASTE BY LEACHING OF LIMONENE

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ABSTRACT

In this paper, it was demonstrated that orange peel waste is a potentially valuable resource that can be developed into high-value products such as ethanol. Following a pre-treatment to extract D-limonene, the anaerobic digestion of orange peel waste was evaluated at laboratory and pilot scale under mesophilic and thermophilic conditions. D-Limonene removals of 70% were reached with pre-treatment. The results showed the convenience of thermophilic conditions for treating this waste, as the ethanol production rate and biodegradability were higher than at mesophilic temperature. At the pilot scale, a thermophilic continuously stirred-tank reactor working in semi-continuous mode was employed. The OLR was found to be in the range of 1.20–3.67 kg COD/m3 d; the most appropriate range for working under stable conditions at SRT of 25 d. The ethanol yield coefficient was found to be 0.27–0.29 LSTP CH_4/g added COD, and the biodegradability 84–90% under these conditions. However, acidification occurred at the highest OLR.

1. INTRODUCTION

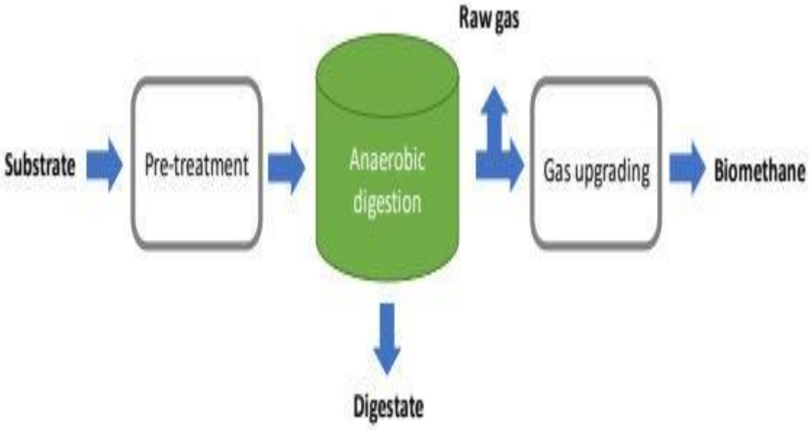
The world is facing many environmental problems connected to human activities. Global warming is probably the best known and is caused by emissions of greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). In the Paris Agreement (UNFCCC, 2015), which entered into force in November 2016, the goal of a limited global temperature increase of 2˚C relative to pre-industrial levels was reaffirmed. As of February 2020, 189 of 197 parties have ratified the agreement (UNFCCC, 2020). According to a report from the IPCC (Intergovernmental Panel on Climate Change), global warming is accelerating, and the rise in temperature should be stopped at 1.5˚C instead. One way to reduce global warming would be to reduce emissions of, for example, CH_4, which has 25 times the impact of CO_2 on global warming.

Besides global warming, there are also increasing global problems relating to eutrophication. The acidification of soils can lead to decreasing soil quality and reduced crop yields. Acidification in oceans is a result of more CO2 dissolving in the water, thus lowering the pH, which affects, for example, corals. Eutrophication is occurring in many of the world's lakes, coastal areas, and rivers and is mainly caused by emissions of nitrogen and phosphorus. The UN's 17 Sustainable Development Goals (SDGs), which were adopted by all members of the United Nations in 2015, are the blueprint for a more sustainable future (UNDESA, 2015). The SDGs include, for example, life on land, climate action, and affordable and clean energy. According to Bhatta (2018), biogas can contribute to eight of the SDGs, while the World Biogas Association (2017) estimates that biogas can contribute to nine of the SDGs. However, Hagman and Eklund (2016) claim that biogas can contribute to all 17 of the SDGs.

The main purpose of producing biogas through anaerobic digestion of organic material is often to produce a renewable energy carrier that can replace fossil fuels. The European Union has launched targets for 2030 of reducing GHG emissions by 40%, relative to 1990 levels, and achieving a proportion of at least 27% renewables in the energy system. Biogas can contribute to fulfilling both of these targets. Anaerobic digestion is also a sustainable waste management option for organic waste, in contrast to landfilling. In the European Union, Directive 1999/31/EU on the landfill of waste establishes a goal of reducing biodegradable waste sent to landfill. An amendment to the Directive states that all waste suitable for recovery or recycling should not be landfilled by 2030. Directive 2008/98/EC on waste presents the waste management hierarchy, an order of prioritization for waste management. At the top of the hierarchy is the prevention of waste, followed by reuse, recycling, recovery, and, at the bottom, disposal (landfilling). The remaining solid material after anaerobic digestion is called digestate and is rich in nutrients and can be used as fertilizer on farmlands.

Thus, anaerobic digestion corresponds to the recovery level, since both energy and nutrient recovery are possible with biogas production systems.

Biogas production occurs when organic materials are degraded by microorganisms in an anaerobic environment. Biogas primarily consists of methane (CH_4) (50-75%) and carbon dioxide (CO_2) (25-50%). Other components of biogas include water (H_2O), oxygen (O_2), sulfur (S), and hydrogen sulfide (H_2S). The digestion process occurs in four distinct stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. To maintain a stable anaerobic process, all four stages should be present simultaneously. The energy carrier in biogas is methane, which is produced during the methanogenesis stage. Figure 1 provides a simplified overview of a biogas production system.

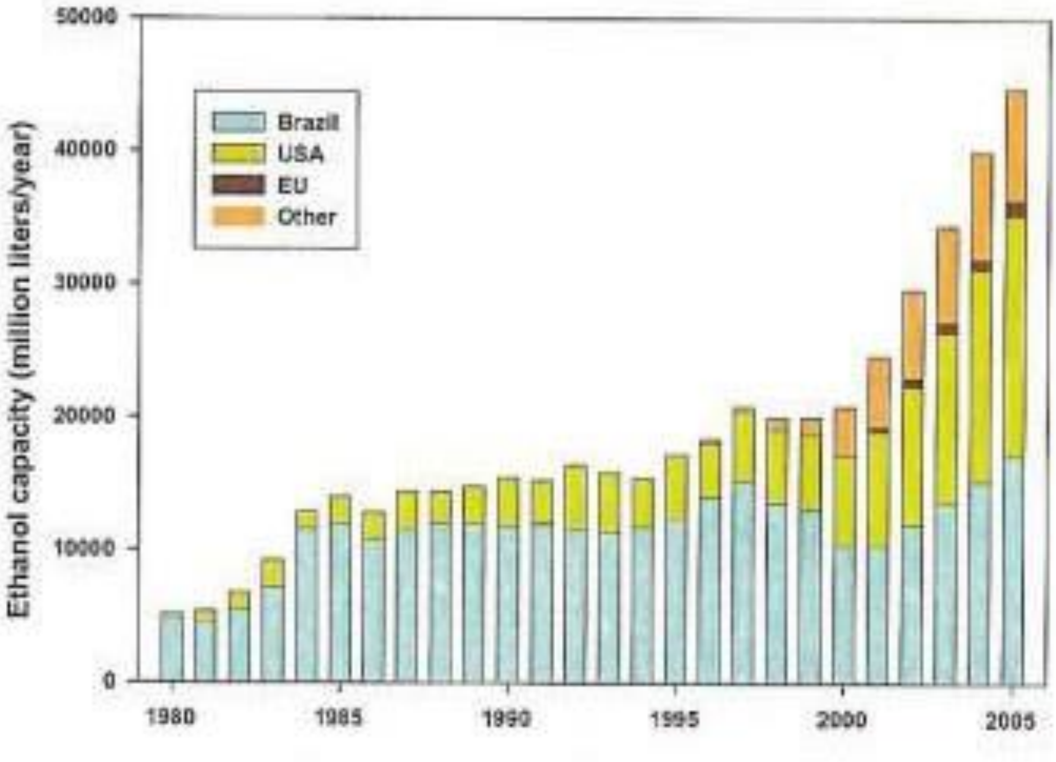


Various organic materials serve as substrates (inputs) for the biogas production process. Common substrates include food waste from households and restaurants, industrial waste from the food processing industry and slaughterhouses, sludge from wastewater treatment plants, manure, and other residues from the agriculture sector. Depending on the composition of the substrate used, different pre-treatment technologies are needed to prepare the substrate for digestion in the digesters at biogas plants. Pre-treatment may involve crushing or grinding to reduce the size of the material, diluting to make the substrate more volatile, and removing unwanted materials such as plastics, textiles, metals, or gravel.

Anaerobic digestion can be performed at different temperatures, most commonly at mesophilic (35-40˚C) or thermophilic (55-60˚C) temperatures. The temperature influences the degradation of the organic material as well as the stability of the process. A thermophilic process has a higher degradation rate, and a shorter retention time may therefore be required.

Fuel Ethanol

Currently, the fuel market dominates the ethanol market. Over the past quarter-century, the focus has been on producing fuel ethanol as a substitute or additive to gasoline. In gasoline, ethanol provides supplementary oxygen in the combustion process, improving combustion efficiency. The growing interest in fuel ethanol depends on a combination of factors such as environmental, social, and energy security issues. The dominant producers and consumers worldwide are Brazil and the USA. Additionally, over 30 countries have introduced, or are interested in introducing, agendas for fuel ethanol.



2. Literature Review

The author delineates the production of ethanol from municipal and industrial waste. These wastes undergo anaerobic digestion to produce ethanol gas, effectively minimizing atmospheric pollution by utilizing ethanol from solid waste [1]. Additionally, ethanol emissions from cattle and ruminant livestock are addressed, aiming to reduce atmospheric ethanol levels to mitigate global warming [2]. Moreover, the author investigates the ethanol conversion rates of various fruits and their parts, highlighting mango peels and citrus waste as significant ethanol sources [3].

Furthermore, the extraction of ethanol from ethanol hydrate using lasers is explored, with a focus on the chemically pumped oxygen-iodine energy transfer laser (COIL) as the most effective extraction method [4]. The potential of reducing ethanol and nitrous oxide emissions to mitigate greenhouse gas emissions is proposed, alongside an economic analysis of various techniques utilizing ethanol and nitrous oxide as alternative sources [5].

Additionally, the bio-gas production potential of cotton wastes is discussed, with experiments revealing ethanol yields from anaerobic digestion of cotton stalks, seed hulls, and oil cakes [6]. Predictive methods for estimating ethanol generation in tropical landfills are outlined, highlighting discrepancies between laboratory and field results due to moisture content [7].

Coal mine ethanol (CMM) production, extraction, and optimization are explored, emphasizing the need for optimized designs and comprehensive data for efficient extraction [8]. Moreover, an integrated rotary drum reactor (RDR) is presented for converting municipal waste into biogas, with future enhancements aimed at increasing performance through improved liquid circulation rates [9].

Furthermore, ethanol extraction from jatropha de-oiled cake and orange peel in anaerobic digesters is investigated, yielding significant gas production containing ethanol, carbon dioxide, and carbon monoxide [10]. Lastly, the anaerobic digestion of cow dung is explored, with mesophilic anaerobic digestion yielding substantial ethanol production [11].

Objectives

1. To anaerobically biodegrade each sample of orange peel waste to generate biogas.
2. To assess the biogas potential of different wastes and determine which waste exhibits higher potential.
3. To determine the total solid and volatile solid content of the waste samples.

3. Methodology: Materials and Methods

The following materials, equipment, and experimental procedures were utilized:

Materials:

- PVC pipe (¾ inch)
- T-tube
- Valve
- Tyre tube
- 20-liter C-way bottle
- 500ml incubation bottles
- Feedstocks: Orange peels and inoculum

- Glassware: Petri dishes, crucibles, volumetric flask, measuring cylinder, stirring rod, and beaker
- Chemicals: Distilled water, sodium hydroxide (NaOH), potassium dihydrogen phosphate ($KH2PO4$), dipotassium hydrogen phosphate ($K2HPO4$), magnesium sulfate heptahydrate ($MgSO4$.$7H2O$), potassium chloride (KCl), cobalt (II) chloride ($CoCl2$), nickel (II) chloride ($NiCl2$), potassium hydroxide (KOH), calcium chloride ($CaCl2$), and iron (II) chloride ($FeCl2$)

Equipment:

- pH meter (Hanna Educational HI 208)
- Weighing balance
- Thermometer
- Digester
- Desiccator
- Oven (Drying oven DHG 9030A)
- Furnace (Fritsch DD 3305A)

Method of Analysis: Physical characteristics such as pH, total solids (Ts), volatile solids (Vs), moisture content, and ash content were analyzed according to standard methods (APHA – AWWA 1992) as appropriate.

Digester Set-Up: A digester, also known as an anaerobic digester or biogas plant, provides internal conditions for various chemical and microbiological reactions. Digestion was conducted in a 500 ml plastic container, where 12 g of dried food and fruit waste were mixed with 110 cm3 of non-growth medium and 290 cm3 inoculum to create a slurry of about 450 ml. The mixture was stirred to ensure homogeneity and labeled accordingly, then subjected to anaerobic digestion for a 30-day retention period. Biogas was collected using a water displacement set-up.

Preparation of Non-growth Medium: The non-growth medium was prepared using compounds such as potassium dihydrogen phosphate, dipotassium hydrogen phosphate, magnesium sulfate heptahydrate, calcium chloride, iron (II) chloride, potassium chloride, cobalt (II) chloride, and nickel (II) chloride. The required amounts of each reagent were measured using a top digital high precision balance to provide essential nutrients required by microorganisms.

Pilot System: A case study was conducted using a 20-liter digester to assess the efficacy and quantity of biogas yield as feedstock quantity increased. This pilot system aimed to make biogas production accessible at a household level, utilizing post-anaerobic residue as inoculum to generate more biogas and add value to the overall system.

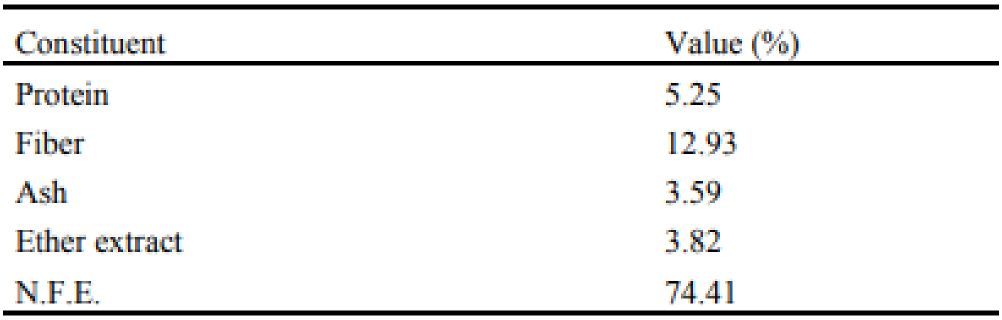
Fig : Digester set up

Fig : Measurement of the biogas using water displacement method

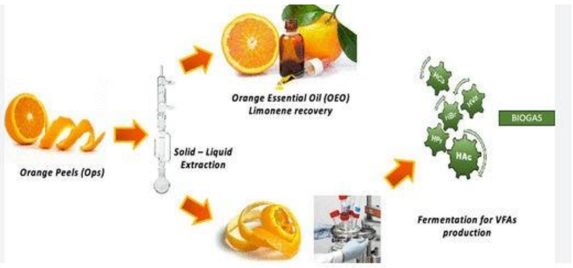
Orange Peel Waste

Citrus fruits comprise an important group of fruit crops manufactured worldwide. In the fruit processing industry, large amounts of waste materials are produced in the form of peel, pulp, seeds, etc. The waste material presents significant disposal difficulties, and when not used in any way, it causes odor and soil pollution. Since the 1980s, the worldwide production of citrus has increased drastically. Estimations show that in 2010, orange production will reach 66.4 million metric tons, which is a 14% increase compared with that of 1997-1999. Almost half, 30.1 million metric tons of the produced orange, will be manufactured to yield juice, essential oils, and other by-products. When dried, citrus peels are rich in cellulose, hemicelluloses, proteins, and pectin, but the fat content is low (see Table 2.3.1). In the citrus processing industry, citrus peels are the major solid by-product and comprise around 50% of the fresh fruit weight. Citrus waste can be used as raw material for pectin extraction or in pelletized form for animal feeding. However, the citrus waste has to be dried first, and none of these processes has been found to be very profitable. A disadvantage is that orange peels have a very low nutritional content which reduces its value as livestock feed.

Table: Nutritional Composition of Mexican Orange Peels



Constituent	Value (%)
Protein	5.25
Fiber	12.93
Ash	3.59
Ether extract	3.82
N.F.E.	74.41



Limonene and Orange Peel

The peels are usually disposed of by burning, producing carbon dioxide and other greenhouse gases, or dumping into landfills, where the waste from rotting peels percolates into the soil, harming plant life. This includes the orange peel or rind, which upon extraction, yields an oil that typically contains more than 90% of an organic compound called limonene.

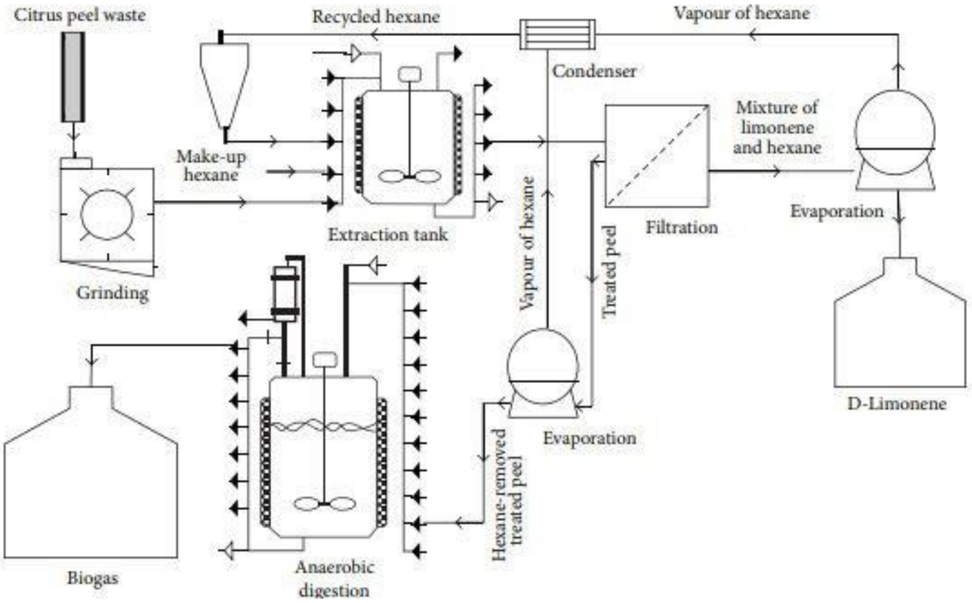


Figure : Block flow diagram of biogas production from treated orange peel waste by leaching pretreatment and limonene extraction

Experiment 1: Using Pectin and Yeast only to produce Ethanol 400 mL of the obtained pectin was put in a 500 ml conical flask with 2g S. cerevisiae and thoroughly mixed with the liquid pectin. Fermentation was allowed to take place on the mixture for 14 days using ambient temperature. Distillation was used to separate the mixture.

Experiment 2: Using Pectin and E.coli only to produce Ethanol The same quantity as above was put in a 500 ml conical flask and 2 wire loop E. coli. The mixture was allowed to ferment anaerobically for 14 days. Distillation was used to separate the mixture.

Experiment 3: Using Pectin, E.coli and Yeast The same quantity as above was put in a 500 ml conical flask, hydrolyzed with 2 wire loop E.coli. After 48 hours, 2g S. cerevisiae was added, and the mixture fermented anaerobically for 14 days.

Experiment 4: Control (Pectin only) This experiment used only pectin without any additional agents.

The experimental set-up used at the laboratory scale for the anaerobic digestion of orange peel waste derived from orange juice manufacturing consisted of two 3.5-l continuous stirred-tank reactors (CSTR) with four connections to load feedstock, ventilate the biogas, inject inert gas (nitrogen) to maintain the anaerobic conditions, and remove effluent. The reactor content was stirred using a stirring blade connected to an engine. The temperature was maintained by means of a thermostatic jacket containing glycerol at 37°C for mesophilic experiments and 67°C for thermophilic assays. All of the experiments were carried out in batch mode. The volume of ethanol produced during the process was measured using 2-l Boyle–Mariotte reservoirs connected to each reactor. To remove the CO2 produced during the process, tightly closed bubblers containing a NaOH solution (6 N) were connected between the two elements. The ethanol volume displaced an equal measurable volume of water from the reservoir.

At pilot scale, the experimental set-up consisted of one 3200-l CSTR. The temperature of the CSTR (55°C) was maintained by means of an electrical thermostatic jacket. The top of the CSTR was fitted with a tube through which the biogas was transported to a condenser to remove the moisture. The biogas was then quantified using a flow meter. The reactor was fed in semi-continuous mode (three times a day). After storing the digestate in a buffer tank, a centrifuge was used to separate the solid phase from the liquid phase. An additional tank was used to chop and store the substrate prior to the anaerobic treatment.

For the mesophilic experiments, the reactors were inoculated with methanogenically-active granular biomass obtained from a full-scale anaerobic reactor used to treat brewery wastewater belonging to the Heineken S.A. Factory (Jaen, Spain). The thermophilic experiments were carried out by inoculating biomass from a full-scale anaerobic reactor used to treat vegetable and agricultural wastes from the Colsen b.v. Agency (Hulst, The Netherlands). Table 1 shows the analytical characterization of both types of sludge, which were selected on the basis of their high methanogenic activity (Field et al., 1988). The sludge showed values ranging from 0.87 to 0.99 g COD/g VSS d for mesophilic bacteria and 0.98–1.09 g COD/g VSS d for thermophilic microorganisms.

Raw materials

Bottle

5. RESULTS AND DISCUSSIONS

D-Limonene Extraction

The concentration of D-limonene in the distillate samples (25 mL) was monitored over time, as illustrated in Fig. 1. It was observed that the D-limonene concentration stabilized after 1 hour of distillation, indicating that this duration is economically optimal for reducing the concentration of D-limonene in orange peel waste. The extraction yield achieved with this pre-treatment method for 1 hour was approximately 70%. Around 12.5% of the initially added water was necessary to achieve this yield, equivalent to an energy requirement of 1.7 kJ/g wet orange peel waste.

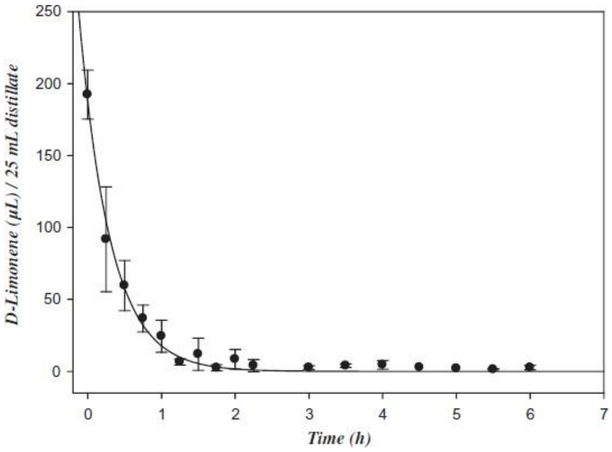


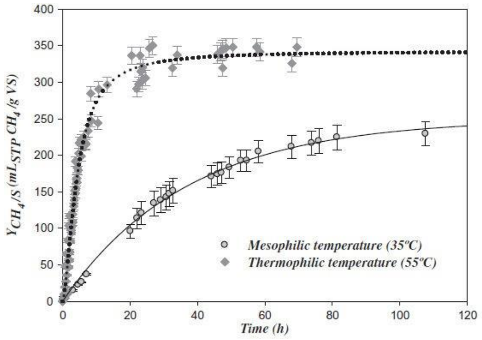
Fig. . Variation of D-limonene concentration in the distillate versus time

Mesophilic and Thermophilic Digestion Viability

Fig. 2 depicts the variation of ethanol yield coefficient from pretreated orange peel waste under mesophilic and thermophilic conditions in batch mode and at laboratory scale. The ethanol yield coefficient at standard temperature and pressure conditions (STP) was found to be higher under thermophilic conditions (332 ± 17 mLSTP CH_4/g added VS) than at mesophilic temperature (230 ± 16 mLSTP CH_4/g added VS). Additionally, the mean rate was considerably different in both cases, being higher under thermophilic conditions (13.28 mLSTP CH_4/g added VS h) than at the lower temperature (1.92 mLSTP CH_4/g added VS h). This indicates that thermophilic digestion is more promising than mesophilic digestion due to its high ethanol production rate, high loading potential, shorter hydraulic retention time (HRT), and consequent reduction of the digester volume, better pathogen and odor control, and weed seed elimination.

Stability

The stability of the anaerobic process is crucial for achieving appropriate energetic valorization of pre-treated orange peel waste. Stability was evaluated based on the evolution of pH, alkalinity, volatile acidity (mg C2/L), volatile acidity/alkalinity ratio (VA/Alk), and volatile fatty acids profile during anaerobic digestion. Table 3 presents the variation of pH and VA/Alk ratio under thermophilic and mesophilic conditions. The pH remained within the optimal range for ethanol-producing bacteria. The VA/Alk ratio, indicating the buffer capacity against acidification, was higher under thermophilic conditions than under mesophilic temperature. These findings suggest that thermophilic conditions are more suitable for revalorizing pre-treated orange peel waste, considering stability, ethanol production rate, biodegradability, and organic loading rate.



Organic Loading Rate (OLR) and Biodegradability

In conclusion, the organic loading rate (OLR) achieved values ranging from 1.20 to 3.67 kg COD/m3 d under stable conditions, with a COD removal efficiency of 84–90%. The highest OLR value that can be reached without acidification and inhibition of ethanol production was found to be 4 kg COD/m3 d. However, when the digester was acidified, the COD removal decreased to 63%. Biodegradability was calculated based on the load added to the reactor and the remaining COD in the liquid phase of the digestate. These values were higher compared to mesophilic conditions, with biodegradability ranging from 74.4% to 58.6%. In previous mesophilic assays at laboratory scale, the biodegradability of pre-treated waste was found to be 65%. After thermophilic anaerobic digestion, the remaining soluble COD in the liquid phase of the digestate was still high for disposal and contained elevated concentrations of nitrogen and phosphorus. Considering that the orange juice plant wastewater has a high content of biodegradable organic matter but low nitrogen and phosphorus content, one possibility could be to combine both wastewaters and treat the mixture in an aerobic membrane reactor (MBR). In regions where soil nutrient enrichment is needed, the wastewater effluent mixture can be utilized as liquid fertilizer.

Ethane Yield Coefficient and Biogas Composition

The ethane yield coefficient and biogas composition were not discussed in the provided text. If you require analysis or discussion on these aspects, please provide the relevant information, and I'd be happy to assist you further.

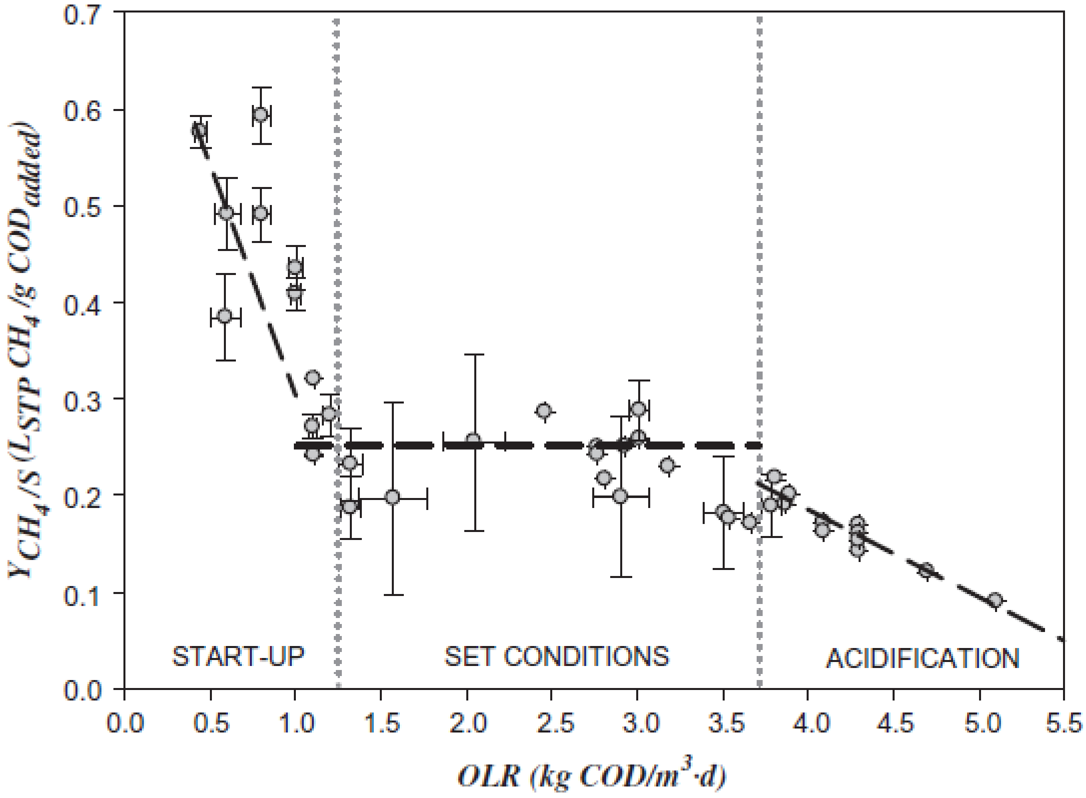


Fig. . Variation of the ethanol yield coefficient with the organic loading rate (OLR) during the thermophilic experiments at pilot scale

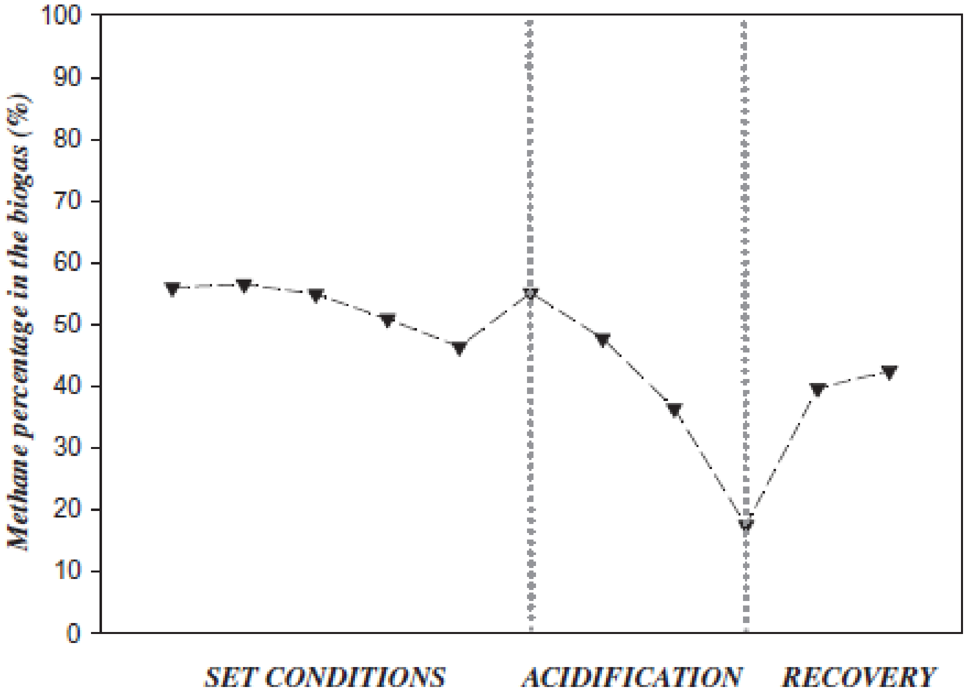


Fig. . Variation of the ethanol percentage in the biogas during the experiments

CONCLUSION

Orange peel waste is a potentially valuable resource that can be developed into high-value products such as ethanol. Following a pre-treatment to extract D-limonene, the anaerobic digestion of orange peel waste was evaluated at laboratory and pilot scales under mesophilic and thermophilic conditions. D-limonene removals of 70% were achieved with pre-treatment.

Anaerobic digestion of orange peel waste after D-limonene extraction revealed higher ethanol production, ethanol production rate, and biodegradability under thermophilic conditions compared to mesophilic conditions. The highest ethanol yield coefficient at pilot scale and thermophilic temperature was 0.27–0.29 LSTP CH4/g added COD, obtained at an OLR of 1.20–3.67 kg COD/m3 d. Biodegradability was found to be 84–90%, although a strong inhibition process was observed when the OLR exceeded 4 kg COD/m3 d, returning to normal levels when the OLR was reduced. Anaerobic digestion provides an excellent opportunity to integrate this waste into a biorefinery approach involved in orange juice manufacturing.

REFERENCES

1. H. G. Bingemer. (1987). The production of ethanol from solid waste. *Journal of Geophysical Research*, 92(D2), 2181-218.
2. K. A. Johnson, & D. E. Johnson. (1995). Ethanol emission from cattle. *The Journal of Animal Science, 73*(10), 2483-2492.

3. V. Nallathambi Gunaseelan. (2004). Biochemical ethanol potential of fruits and vegetable solid waste feedstocks. *Biomass and Bioenergy, 26*, 389–399.

4. Tomoo Fujioka, Kazuya Jyosui, Hiroyuki Nishimura, & Kazuyoku Tei. (2003). Extraction of ethanol from ethanol hydrate using lasers. *The Japan Society of Applied Physics, 42*, 5648–5651.

5. Mitigation of Ethanol and Nitrous Oxide Emissions from Waste, Energy and Industry. (2006). *The Energy Journal.*

6. A. Iscia, & G. N. Demirer. (2007). Biogas production potential from cotton wastes. *Renewable Energy, 32*, 750–757.

7. Sandro L. Machado, Miriam F. Carvalho, Jean-Pierre Gourc, & Orencio M. Vilar. (2009). Ethanol generation in tropical landfills: simplified methods and field results. *Waste Management, 29*, 153–161.

8. Li Guo-jun. (2009). Theoretical research and practice on coal mine ethanol extraction and ground development design. *Procedia Earth and Planetary Science, 1*, 94–99.

9. Baoning Zhu, Ruihong Zhang, Petros Gikas, Joshua Rapport, & Bryan Jenkins. (2010). Biogas production from municipal solid wastes using an integrated rotary drum and anaerobic-phased solids digester system. *Bioresource Technology, 101*, 6374–6380.